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VOLTAMMETRIC DETERMINATION OF ACROLEIN

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16. ABSTRACT

A differential pulse polarographic method was developed for acrolein. It is based on electrochemical reduction of acrolein at the dropping mercury electrode. With this method, acrolein can be quantitated in natural and condenser cooling waters at concentrations of 0.05 to 0.5 mg/l. The sample for acrolein analysis is buffered at pH 7.2 with 0.09 M phosphate to resist changes in pH, and ethylenediaminetetraacetic acid is added in a concentration of 0.09% to prevent interference from zinc. The recovery of acrolein was unaffected by pH in the 6.8-7.6 range and by zinc at 2.0 mg/l. Replicate analyses at concentrations of 0.1 and 0.3 mg/l acrolein in reagent water gave respective standard deviations of 7.2 and 4.1% and relative errors of 2.8 and 3.3%. The recommended method is given in the appendix.

Employing differential pulse voltammetry at the glassy carbon electrode, acrolein was determined with a sensitivity of 10 mg/l. The acrolein was indirectly measured by forming the sulfite complex and oxidately measuring unreacted sulfite in 0.09 M phosphate buffer at pH 7.2.

The effectiveness of sulfite in preserving acrolein could not be evaluated as all attempts failed in quantitatively recovering acrolein at 0.5 mg/l in the presence of excess sulfite.

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ABSTRACT

A differential pulse polarographic method was developed for determining concentrations of acrolein in natural waters and in condenser cooling water. Acrolein is electrochemically reduced at negative potentials at the dropping mercury electrode. The height of the polarographic peak versus the saturated calomel electrode (SCE) is measured and referred to a standard curve. The range of this method is from 0.05 to 0.5 milligrams per liter (mg/l) of acrolein.

Acrolein concentrations can also be determined by differential pulse voltammetry at the glassy carbon electrode. Acrolein is measured indirectly by forming the acrolein-sulfite complex; unreacted sulfite is determined by measuring the oxidizing current at positive potentials in a buffer solution. This procedure does not require lengthy deaeration to remove oxygen, but its poor sensitivity (10 mg/l) makes it less attractive than the polarographic method.

Acrolein formed a complex with sulfite and could not be recovered at 0.5 mg/l from samples preserved with excess sulfite.

This report was submitted by the Tennessee Valley Authority, Division of Environmental Planning, in partial fulfillment of Energy Accomplishment Plan 78BDH under terms of Interagency Energy Agreement D6-E721 with the Environmental Protection Agency. Work was completed as of July 1975.

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SECTION I

CONCLUSIONS

With a method based on electrochemical reduction at the dropping mercury electrode, acrolein can be determined at concentrations between 0.05 and 0.5 mg/l in both natural waters and in condenser cooling water by differential pulse polarography (voltammetry at the dropping mercury electrode). The sample for acrolein analysis is buffered at pH 7.2 with 0.09 mole per liter (molar, M) phosphate, and ethylenediaminetetraacetic acid (EDTA) is added in a concentration of 0.09 percent (%) to prevent interference from zinc. The height of the peak current at about -1.2 volts versus a calomel electrode filled with saturated sodium chloride [V vs. S.C.E. (NaCl)] is compared with a standard curve. The recovery of acrolein is unaffected by changes in pH between 6.8 and 7.6 or by concentrations of zinc as high as 2.0 mg/l. Replicate analyses showed that acrolein could be determined accurately at concentrations of 0.1 and 0.3 mg/l with standard deviations of 0.008 and 0.013 mg/l, respectively. The recommended method is given in the appendix.

Differential pulse voltammetry at the glassy carbon electrode allows the determination of acrolein with a sensitivity of 10 mg/l. Acrolein is reacted with excess sulfite, and the unreacted sulfite is determined by measuring the oxidizing current at +0.6 V vs. S.C.E. (NaCl) in 0.09 M phosphate at pH 7.2. Although this method does not require extensive deaeration, it is less sensitive than the recommended method.

Sulfite, which forms a complex with acrolein, was tested as a preservative for water samples taken for analysis of low levels of acrolein. However, acrolein could not be recovered from solutions containing excess sulfite; at most, only 15% of the acrolein was recovered. Because attempts to break the acrolein-sulfite complex were not successful, sulfite is not recommended for preserving acrolein.

SECTION II

RECOMMENDATIONS

Differential pulse voltammetry at the dropping mercury electrode (polarography) is the recommended method for determining acrolein at concentrations from 0.05 to 0.5 mg/l in natural or condenser cooling waters. The method is presented in the appendix. This method was studied for analysis of water associated with steam-electric generating stations. It was not within the scope of this project to test its applicability to other industrial and domestic waste waters, but it is recommended that this testing be performed.

Acrolein can also be determined by differential pulse voltammetry at positive potentials at the glassy carbon electrode. Acrolein is reacted with excess sulfite, and the unreacted sulfite is determined by measuring the oxidizing current. Because of the poor sensitivity (10 mg/l), the procedure was not evaluated for analyzing natural and condenser cooling waters. The sensitivity of the technique might be improved with another electrode (for example, the graphite electrode impregnated with styrene and irradiated with cobalt 60). The technique may be applicable to monitoring sulfur dioxide. The information contained herein on the reaction of acrolein with sulfite may be valuable in evaluating, by bioassay, the effect of sulfite in neutralizing acrolein toxicity.

Sulfite is not recommended as a preservative for acrolein solutions because acrolein formed a complex with excess sulfite and could not be recovered by any of the techniques tested.

SECTION III

INTRODUCTION

Acrolein is an olefinic aldehyde with the chemical name propenal. It is registered for use in controlling slime growths. It also has potential for use as a molluscicide for controlling Asiatic clams in the heat exchangers and other service water systems at steam-electric generating stations; however, it is not now registered for this application. Acrolein is toxic, but it is rapidly dissipated in the environment. Knowing the quantity of acrolein dissipated in the test water (acrolein demand) and the dilution factor, one can readily calculate residuals in the environment. Walko[1] discussed the advantages that acrolein has over chlorine for controlling mussels and Asiatic clams.

Sensitive and rapid analytical methods that are accurate and precise are needed for monitoring acrolein in the environment. A number of methods have been devised for measuring concentrations of acrolein.

Cohen's[2] spectrophotometric method, which traps acrolein in the colorimetric reagent 4-hexylresorcinol, is the standard for measuring concentrations of acrolein in air, and it is approved by the Intersociety Committee[3] as a tentative method. At the Betz Laboratories, this method is used for determining acrolein in water.[4] The acrolein is separated from water by distilling it into the colorimetric reagent; the sample is then visually compared with standards. Spectrometric measurement[5] can be used instead of visual comparison.

For acrolein concentrations near 0.3 mg/l, the dosage that has been used to control slime growths and that may be useful for controlling infestations of Asiatic clams,[1] the Betz Laboratories method frequently produced erratic results. Furthermore, the distillation and color

development steps were time-consuming. Therefore, TVA searched the literature for a better method.

Verhaar[6] used gas chromatography to determine acrolein concentrations in the combustion products of propylene. Smythe[7] determined acrolein concentrations in diesel engine exhausts by means of a gas chromatographic procedure based on the volatility of the hydrazone derivative of acrolein. These methods have not been applied to the determination of acrolein concentrations in water.

One reported colorimetric method[8] measures the absorbance of the hydrazone derivative to determine concentrations of acrolein in water. This method, although adequately sensitive, is very time-consuming.

Moshier[9] reported a polarographic method for assaying acrolein in water with a detection limit of 10 mg/l. Van Sandt[10] improved Moshier's method to achieve a detection limit of 1 mg/l, but this sensitivity is still not sufficient for monitoring an acrolein concentration of 0.30 mg/l.

With differential pulse polarography, an extremely sensitive and economical analytical tool,[11] it should be possible to improve the sensitivity of the Van Sandt method[10] to 0.05 mg/l. The theory and practice of differential pulse polarography are given in the literature.[11-17]

One difficulty in the use of low-level polarographic analysis is the interference of dissolved oxygen.[18] Oxygen must be removed by sparging with nitrogen that has been scrupulously purified to remove all traces of oxygen.

Lengthy deaeration, however, is unnecessary at potentials greater than about +0.1 volts versus a calomel electrode filled with saturated potassium chloride (V vs. S.C.E.). At positive potentials, the mercury electrode is analytically worthless,[18] but the glassy carbon electrode produces suitable results.[19] Tables of the voltammetric behavior of organic compounds at solid electrodes[20] contain no information on the direct determination of acrolein by oxidation at positive potentials. An indirect determination involving coulometry with bromine is reported,[21] but this method is not specific for acrolein.

These findings suggested an investigation of the voltammetry of acrolein using the glassy carbon electrode. A possible approach to the electroanalysis of acrolein, not mentioned

in the literature, could be based on the acrolein complex with sulfite.[1,22,23] Either a direct determination of the complex, should it prove to be electroactive, or an indirect measurement of unreacted sulfite might be possible.

The electrochemical behavior of sulfite at the glassy carbon electrode has not been investigated, nor has the behavior of the acidic forms of sulfite (bisulfite and sulfur dioxide). Theoretically, sulfite should oxidize readily at the carbon electrode, because its standard potential in base is +0.69 V vs. S.C.E.[21] Sulfur dioxide, the conjugate acid of sulfite, is electrochemically active at the platinum membrane electrode.[20] The voltammetric determination of sulfur dioxide by coulometric generation of bromine at positive potentials is well known,[21] and instruments for monitoring sulfur dioxide in air have been based on that principle.[24,25] Sulfur dioxide has been determined by differential pulse polarography in nonaqueous solvents.[26]

Because acrolein readily decomposes, even when preserved with 0.1% weight expressed as a fraction of total volume (w/v) hydroquinone,[22] samples with acrolein must be analyzed immediately. About one-third of the acrolein at the 1.0-mg/l level in a sealed volumetric flask filled to the mark is lost within 4 days.[1] Jackson[27] suggested sulfite at pH 7 as a potential preservative for low levels of acrolein, about 0.5 mg/l and below, and regeneration of the acrolein for analysis by distillation at pH 1 or 13. Sulfite in a concentration of 1% (w/v) sodium bisulfite plus refrigeration at 6 degrees Celsius (°C) is a known method for preserving high levels of acrolein, about 2 mg/l and above, in aqueous solutions impinged from air.[28]

Based on the foregoing literature review, the goals of this research were (1) to develop a method capable of determining acrolein in concentrations as low as 0.05 mg/l by differential pulse voltammetry with the dropping mercury electrode (polarographic method) at negative potentials after removing oxygen; (2) to develop a voltammetric method for determining acrolein, either directly or indirectly with sulfite, with the glassy carbon electrode at positive potentials without removing oxygen; and (3) to test the effectiveness of sulfite as a preservative for acrolein in solution at the 0.5-mg/l level.

SECTION IV

EXPERIMENTAL

APPARATUS

All measurements were made with the Princeton Applied Research (PAR) Model 174 Polarographic Analyzer with mechanical drop timer and Houston Omnigraphic X-Y Recorder Model 2200-3-3. The dropping mercury electrode was a 2- to 5-second capillary from Sargent-Welch Company with Part No. S-29419. The glassy carbon electrode was obtained from PAR, as were the carbon counter electrode, the salt bridge with isolation frit, the saturated calomel electrode, the outgassing tube, the cell holder, the cell, and other electrochemical accessories.[19]

Nitrogen gas used to deaerate solutions for polarographic analysis was purged of oxygen. Zero-grade nitrogen gas was passed through a furnace containing a special catalytic converter (Model 02-2315 Gas Purifier purchased from Supelco, Bellefonte, Pennsylvania) and heated to 600°C. The gaseous effluent from the furnace was successively passed through a Hydro-Purge unit and a Dow gas purifier, both of which are available from Applied Science Laboratories, State College, Pennsylvania. The gas was then passed through sintered glass frits in three scrubbing towers, two containing 100 milliliters (ml) of 0.1 M chromous chloride in 2.4 M hydrochloric acid with amalgamated zinc and one containing 100 ml of reagent water. The amalgamated zinc was 0.8-3.2 millimeter (mm) pore size for a Jones reductor (Fisher Scientific Company, Fairlawn, New Jersey). Details for preparing the chromous chloride scrubbers are given by Meites.[18]

REAGENTS

All chemicals were reagent grade and, except for acrolein, were used without further purification. Reagent water was used throughout this study. It was dispensed from a Super-Q system manufactured by Millipore Corporation, Bedford, Massachusetts. The system purifies tap water by filtration, adsorption on activated carbon, mixed-bed ion exchange, and final filtration through a 0.8-micrometer (μm) membrane filter.

Purification and Assay of Acrolein

The acrolein used in this study was distilled, and the fraction that boiled at 51-53 °C was collected in sufficient hydroquinone to provide a final concentration of 0.1% w/v hydroquinone.

> CAUTION
>
> Acrolein is a powerful lacrimator and irritates the skin. Handle with gloves in a ventilated hood. Acrolein also, when hot and concentrated, may react explosively with oxidants, bisulfates, or other chemicals. It is also very flammable.

The acrolein in the clear distillate was assayed with bisulfite.[23] As detailed by Siggia,[23] the bisulfite was generated in a 500-ml glass-stoppered Erlenmeyer flask by adding, while the contents were being stirred, 50 ml of standard 1 N sulfuric acid to 250 ml of 1 M sodium sulfite. About 1.2 grams (g) of the raw acrolein was accurately weighed into the flask with a weighing pipet. The flask was tightly stoppered and shaken for 5 minutes to complete the reaction of acrolein with the bisulfite. The unreacted bisulfite was potentiometrically titrated with standard 1 normal (N) sodium hydroxide. The end point, found in these studies, appeared at pH 9.5. Potentiometric titration and use of equation (1) revealed that one bisulfite molecule formed a complex with each molecule of acrolein. This information and the end point are not given in the literature.[22,23] The percentage of acrolein was calculated according to

$$\text{Acrolein, \%} = \frac{(V_1 - V_2) \times N \times 56.06}{W \times 10} \qquad (1)$$

where V = standard 1 N sodium hydroxide required to titrate 50.0 ml of standard 1 N sulfuric acid in the excess sulfite (milliliters)

V = standard 1 N sodium hydroxide used to titrate the sample (milliliters)

N = normality of standard 1 N sodium hydroxide

W = weight of acrolein taken for analysis (grams)

Reagent-grade acrolein was cloudy and contained about 65% acrolein by bisulfite assay, whereas the freshly distilled product inhibited with 0.1% w/v hydroquinone contained about 93% acrolein and was clear. Assay results are presented in table 1.

TABLE 1. BISULFITE ASSAY RESULTS FOR ACROLEIN

Source	Appearance	Acrolein content, %
Eastman (distilled)	Clear	92.7 (average of 3 tests)
Eastman (as received)	Cloudy	67.7
Baker (as received)	Cloudy	64.9

Acrolein was also assayed by an infrared technique[29] based on the relative absorbances of bands attributable to the acrolein dimer (2-formyl-3,4-dihydro-2H-pyran): an ortho-substituted phenyl band at 13.6 μm and an ether band at 9.35 μm. The infrared assay revealed that the acrolein as received contained about four times more total impurities, mainly the dimer (also called disacryl), than the freshly distilled product, thereby confirming the bisulfite assay. Infrared spectra indicated that the unidentified precipitate found in the acrolein as received contained little, if any, disacryl. This suggests that the dimer is a soluble

material that gradually forms even in freshly distilled acrolein.

Another method for assaying acrolein was suggested by James.[30] This method is based on brominating the double bond in acrolein and titrating the excess bromine with standard thiosulfate. Had this method been used, it would have indicated higher concentrations of acrolein than were actually present because of interference from disacryl, which has a double bond that consumes bromine. On the other hand, the formyl group in disacryl probably does not interfere in the bisulfite assay because it is chemically similar to furfural, which is known not to interfere.[23]

Acrolein Stock Solution

To prepare a stock solution of acrolein, about 1 g of purified acrolein (weighed to the nearest 0.01 g) was dispensed from a weighing pipet into reagent water in a 1000-ml volumetric flask. The solution was diluted to 1 liter (l). The concentration of acrolein in the stock solution was calculated in milligrams per milliliter, taking into consideration the acrolein content found by bisulfite assay. This solution must be prepared fresh daily.

Acrolein Standard Solution

A standard solution of acrolein was prepared by appropriate dilution of the stock solution to 100 mg/l.

Phosphate Buffer Solution

The 1.0 M phosphate buffer solution, pH 7.4, was prepared by mixing 300 ml of 1.0 M dipotassium hydrogenphosphate (174.18 g/l) and 100 ml of 1.0 M potassium dihydrogenphosphate (136.09 g/l). Table 2 gives the preparation of phosphate buffer solutions used to test the effects of pH on the polarographic behavior of acrolein.

EDTA Solution

A 10% (w/v) EDTA solution was prepared by dissolving 25 g of disodium ethylenediaminetetracetic acid dihydrate and diluting to 250 ml with reagent water. Dissolution was completed by magnetically stirring the solution while

TABLE 2. PREPARATION OF PHOSPHATE BUFFER SOLUTIONS FOR TESTS OF THE EFFECTS OF pH ON POLAROGRAPHIC DETERMINATION OF ACROLEIN

Phosphate (KH_2PO_4), ml pH 4.2	pH 9.3	Combined pH of Mixed or Unmixed Phosphate Buffer	pH of 10.0 ml of Water with 0.5 mg/l Acrolein and 100 µl of 10% EDTA in 1.0 ml of Phosphate Buffer
0	X	9.3	8.3
2.5	17.5	7.8	7.6
5.0	15.0	7.4	7.2
10.0	10.0	6.7	6.8
X	0	4.2	4.3

heating it in a hot water bath. After a Whatman No. 30 filter paper was rinsed with two 25-ml aliquots of reagent water, two 5-ml aliquots of the solution were filtered through it and discarded, and the remaining solution was filtered and saved.

Sodium Sulfite Solution

A 1-M sodium sulfite stock solution was prepared by dissolving 255.935 g of 98.5% sodium sulfite (Na_2SO_3) in reagent water and diluting to 2000 ml. A 17.85-ml aliquot of this solution was diluted to 100 ml to yield a 22,500-mg/l solution. This solution was diluted further to give a 225-mg/l solution, 1 ml of which is equivalent to 100 µg of acrolein because, as found by bisulfite assay, one molecule of sodium sulfite forms a complex with each molecule of acrolein.

PROCEDURE

Voltammetry at Negative Potentials with the Dropping Mercury Electrode (Polarography)

For these studies, the PAR polarographic analyzer was adjusted as follows: drop time, 2 seconds; scan rate, 2 millivolts per second (mV/sec); display direction, positive; scan direction, negative; initial potential, -0.900 or -0.500 volt (V); range, 1.5 V; modulation amplitude, 100 mV; operation mode, differential pulse. The Y-axis of the recorder was set at 1 volt per inch (V/in., 0.039 volts per millimeter, V/mm) to provide 10 V full scale, and the X-axis was set at 100 mV/in. (3.94 mV/mm) to provide a range of 1.5 V. The voltage output offset was adjusted negatively, as necessary, to bring the recorder pen on scale, and the microamperage switch was adjusted to values between 0.2 and 2 microamperes (μA) full scale depending on the concentration of acrolein.

The counter electrode was spectroscopic-grade graphite. The reference electrode, a calomel electrode filled with saturated sodium chloride, was isolated from the test solution by a slow-leakage sintered-glass frit in a salt bridge, which contained the same electrolyte as the test solution. Without a salt bridge, a moderately sloping cathodic background made the measurement of the peak heights formed by reduction of the acrolein inexact.

The test solutions consisted of 10.0 ml of the standard or sample to be analyzed; 1.00 ml of phosphate buffer solution (pH 7.4) or other ingredients, such as sulfite, as specified; and 100 microliters (μl) of 10% EDTA solution. The mixture was dispensed immediately into a polarographic cell (5-to 50-ml capacity). The mercury head above the capillary was adjusted to about 45 centimeters (cm) to produce a natural drop time of about 3 seconds in the test solution. The test solutions were deaerated 10 minutes (min) with purified nitrogen. After deaeration, the test solution was electrically connected and allowed to quiesce for about a minute. For best sensitivity it was absolutely necessary to remove all traces of oxygen from the gas used to sparge the test solution.

Voltammetry at Positive Potentials with the Glassy Carbon Electrode

The instrumental parameters for these studies were similar to those for voltammetry at negative potentials with the dropping mercury electrode except that the initial potentials were -0.200 V, the voltammograms scanned positively, and the peaks displayed negatively. The voltage output offset was adjusted negatively, as necessary, to bring the recorder pen on scale, and the milliamperage switch was adjusted, as necessary, to 0.1, 0.2, or 0.5 milliampere (mA) full scale. Voltage scans were usually terminated at about +1.1 V because the background current of the electrolyte itself obscured the voltammogram.

The reference and counter electrodes were those described in the preceding section. The reference electrode was placed directly in the test solution; a salt bridge was not necessary under these conditions. Before each run, the glassy carbon electrode was cleaned for 1 min at +1.0 V vs. S.C.E. (NaCl). This greatly reduced the current background from the electrode itself between -0.2 and +1.1V. After it was cleaned, the electrode was rinsed with reagent water, wiped with a tissue, and rinsed again.

The test solutions are described in the "Results and Discussion" section.

Preservation with Sulfite

In these studies, acrolein solutions were treated with either an excess of sodium sulfite or the chemically equivalent amount. Polarographic measurements were made using the same cell, electrodes, salt bridge, and instrument settings specified in the "Voltammetry at Negative Potentials with the Dropping Mercury Electrode (Polarography)" section, except that the initial voltage settings were changed as mentioned in the "Results and Discussion" section.

The test solutions are described in the Results and Discussion section.

SECTION V

RESULTS AND DISCUSSION

VOLTAMMETRY AT NEGATIVE POTENTIALS WITH THE DROPPING MERCURY ELECTRODE (POLAROGRAPHY)

Experimentation led to the development of a sensitive differential pulse polarographic method for determining concentrations of acrolein in water. In brief, the method involves adding 1.00 ml of 1.0 M phosphate buffer solution and 100 µl of 10% EDTA solution to 10.0 ml of sample, removing dissolved oxygen by sparging with nitrogen for 10 min, and recording the polarogram. The height of the acrolein reduction peak at -1.22 V vs. S.C.E. (NaCl) is measured, and the acrolein concentration is determined from a standard curve prepared by polarographing a series of standard acrolein solutions. The recommended procedure is given in the appendix.

The detection limit of the method was found to be 0.05 mg/l, approximately 20 times the sensitivity obtained by direct-current polarography.[10] The concentration range extends to, or beyond, 0.5 mg/l, the highest level used in determining acrolein demand. With the mercury electrode adjusted to provide a natural drop time of 2.7 seconds in 0.09 M phosphate, standard solutions containing 0.1, 0.3, and 0.5 mg/l of acrolein produced peak currents of 112, 392, and 630 nanoamperes (nA), respectively. No measureable current was observed for a reagent blank. The standard curve produced from these readings is displayed in figure 1. The corresponding polarograms are presented in figure 2.

The precision and accuracy of the recommended method were based on seven replicate analyses of freshly prepared standard solutions containing 0.10 and 0.30 mg/l of acrolein. The standard deviations were 0.008 and 0.013 mg/l, respectively, and the relative standard deviations were 7.1 and 4.3 %. The standard deviation was

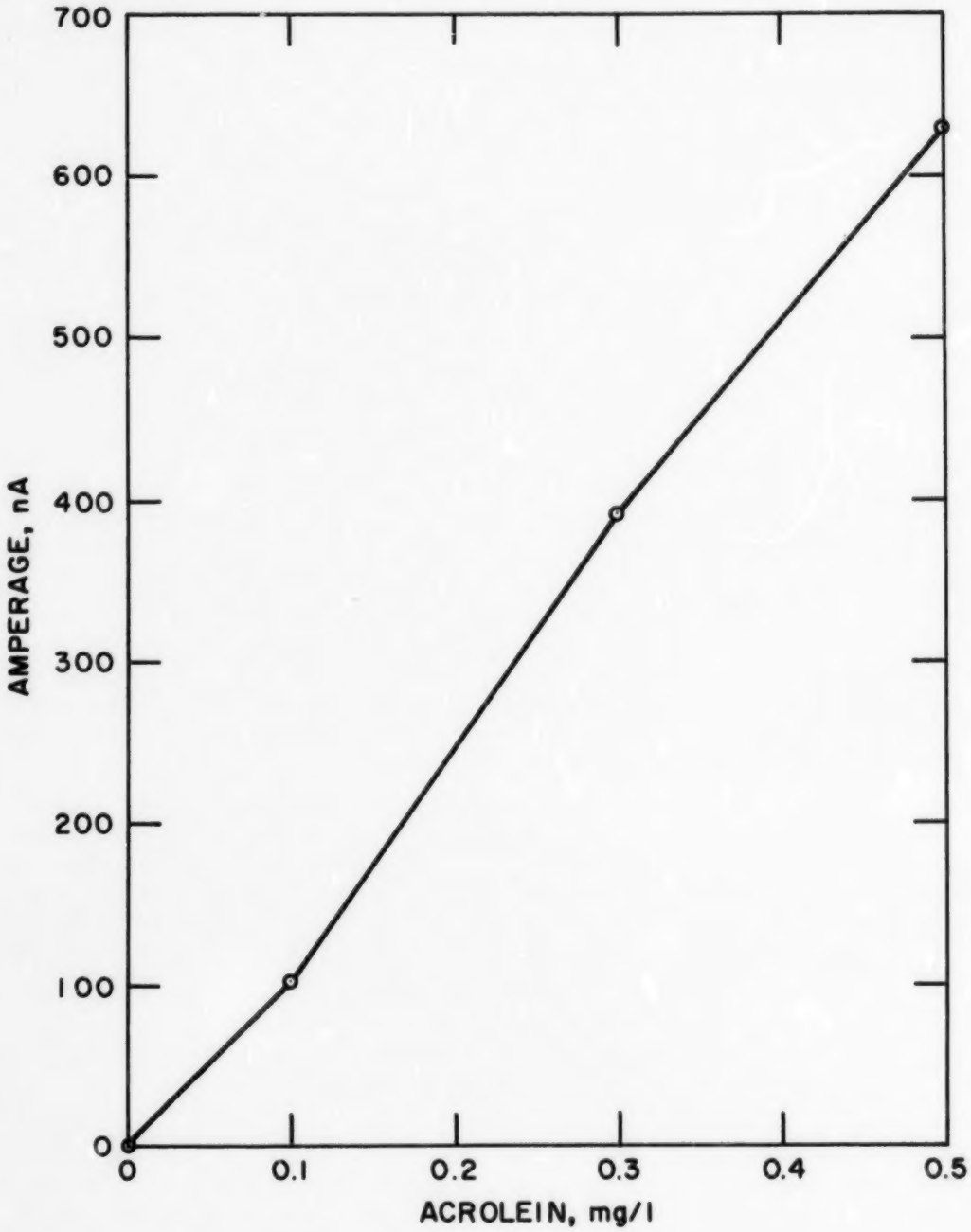


Figure 1. Calibration Curve for Acrolein

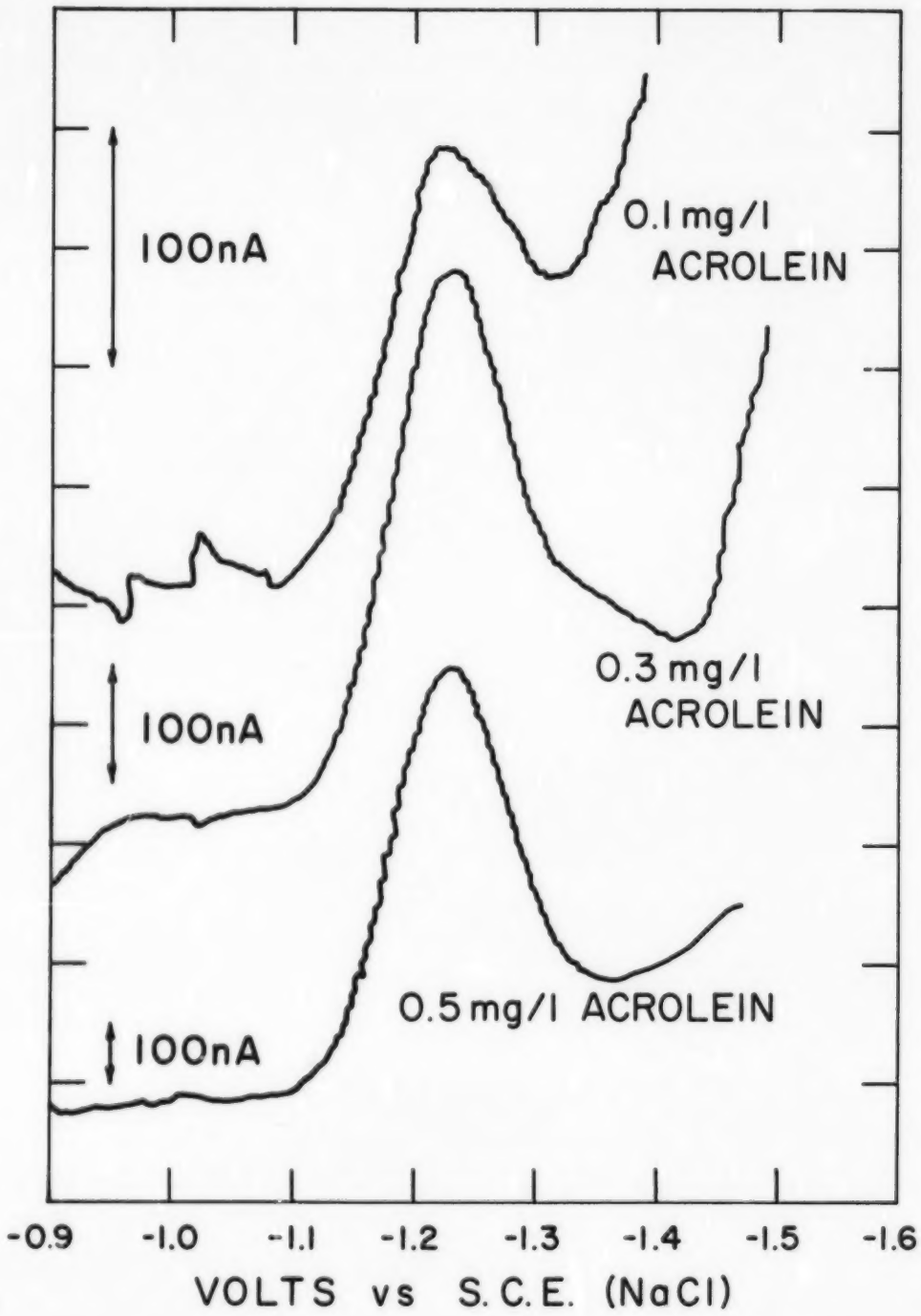


Figure 2. Polarograms for Acrolein with Dropping Mercury Electrode

computed using n-1 for weighting, where n is the number of observations. Recoveries (means of seven determinations) of 0.10 and 0.30 mg/l acrolein were 97 and 97 %, respectively, corresponding to relative errors of 2.9 and 3.3 %.

The polarographic method was compared with the colorimetric method for determining the acrolein demand of samples of water taken in the Tennessee Valley. The colorimetric method is the Betz Laboratories test method[4] with spectrometric determination of absorbance at 600 nanometers (nm).[5] Acrolein demand, which is analogous to chlorine demand,[31] is the difference between the concentration of acrolein added (usually 0.30 mg/l) and that found after a 1-hour test period. Analytical results for acrolein demand after one hour for split samples of surface waters with 0.3 mg/l acrolein added and analyzed by the polarographic and colorimetric methods are given in table 3. According to the paired-sample t test,[32] the mean of the differences ($\bar{d}$) between these observations is not significantly different from zero at the 0.05 level of significance. The t values were calculated by multiplying the mean of the differences by the square root of the paired observations and dividing by the standard deviation for the differences. The standard deviation was computed using n-1 weighting, where n is the number of observations. The t value was 1.30, which is less than that of 1.75 given for $t_{0.05}$ for 15 degrees of freedom in the t table.[32] Thus, at the 0.05 level there is only one chance in 10 of incorrectly concluding that the methods do not differ. Acrolein demand at 0.10- and 0.50-mg/l concentrations was determined by both the colorimetric and polarographic methods. Approximately the same fraction of acrolein was consumed at these levels as at 0.30 mg/l.

Chemical Interferences

Zinc -

Zinc interfered in the polarographic determination of acrolein in the 0.09 M phosphate buffer solution (pH 7.4) by causing a high current at -1.22 V vs. S.C.E. (NaCl). The background current in samples that contained 2.0 mg/l of zinc was about four times that for 0.5 mg/l of acrolein. This is important because many natural waters contain as much as 2.0 mg/l zinc. However, the interference of 2.0 mg/l of zinc was completely eliminated by the addition of 0.09% EDTA in the electrolyte. It is well known that 3% EDTA eliminates electrochemical interference by zinc.[33] However, it was not known that lower concentrations of EDTA

TABLE 3. COMPARATIVE TEST RESULTS FOR ACROLEIN DEMAND AFTER HOUR FOR SPLIT SAMPLES OF SURFACE WATERS WITH 0.30 mg/l ACROLEIN ADDED

Location	Acrolein demand, mg/l	
	Polarographic	Colorimetric
Duck River Mile 133.92	0.09	0.11
Duck River Mile 156.51	0.13	0.03
Duck River Mile 64.0	0.11	0.01
Duck River Mile 47.9	0.08	0.07
Holston River Mile 131.5	0.08	0.11
Holston River Mile 118.4	0.08	0.14
Paradise Tower Inlet	0.15	0.10
Paradise Tower Outlet	0.09	0.16
Holston River Mile 118.4	0.13	0.15
Holston River Mile 131.5	0.13	0.09
French Broad River Mile 54.3	0.16	0.12
French Broad River Mile 77.5	0.10	0.06
French Broad River Mile 71.4	0.12	0.14
Nolichucky River Mile 5.3	0.07	0.09
Cumberland River Mile 285	0.07	0.01
Tennessee River Mile 391.2	0.11	0.03

The Paradise Tower is located along the Green River, which discharges into the Ohio River.

could be used in high-sensitivity polarography for the dual purpose of eliminating interference by zinc and contaminants in the EDTA itself.

Other Elements -

Other elements besides zinc might interfere in the determination of acrolein. These may appear in the polarogram as a peak at a voltage near that for acrolein or as a cathodic background with a positive or negative slope. If this should occur, the amperage peak for a blank of raw sample water may be determined and subtracted from that for the sample with added acrolein. This correction can be more precisely performed digitally with a microprocessor-controlled polarograph (Princeton Applied Research Model 374 Polarographic Analyzer System). In these studies, this was not necessary for the more than 50 samples taken throughout the TVA water system and analyzed by the recommended method.

If the background should be such that the current for the blank is much greater than that for acrolein, the acrolein can be separated by distillation,[4] and the distillate can be analyzed polarographically by the recommended method. In one test of the distillation procedure, we sparged nitrogen at 100 ml/min for 20 min through a synthetic sample heated in a boiling water bath, trapped the acrolein released in 20 ml of reagent water instead of colorimetric reagent,[4] and analyzed the distillate polarographically. The concentration of acrolein in the distillate was about 2-1/2 times that in the original sample. We expected a 5-fold increase from the ratio of sample volume to distillate volume. Specifically, when 0.50 mg/l acrolein in 100 ml of reagent water was distilled with nitrogen, 46% of the acrolein was found in the 20 ml of distillate, 6% remained in the residue, and by difference 48% was lost, presumably by polymerization or to the atmosphere. Van Sandt[10] found approximately the same loss when acrolein was collected on silica gel and eluted for polarographic analysis. It should be noted that distillation concentrates the sample and thereby decreases the detection limit at least 2-1/2 fold.

pH -

The pH of the test solution affects both peak height and potential. The optimum pH is 7.2. Tests were conducted at 22°C with 0.50 mg/l acrolein solutions at pH 4.3, 6.8, 7.2, 7.6, and 8.3, buffered with phosphate solutions (0.09 M)

with 0.09% EDTA added (table 2). The height and potential of the acrolein reduction peak were the same at pH 6.8, 7.2, and 7.6. The pH of most water samples can be adjusted and maintained at pH values between 6.8 and 7.6 by the addition of 1.0 ml of 1.0 M phosphate buffer solution (pH 7.4) and 100 µl of 10% EDTA solution to a 10.0 ml sample. Adjustment may be required for strongly acidic samples, such as drainage from strip mines.

At pH 4.3 the peak height for 0.50 mg/l acrolein was 45% of the value at pH 7.2, and the potential was -1.10 V vs. S.C.E. (NaCl) rather than -1.22 V. These shifts of peak potential and peak height found by differential pulse polarography agree with Moshier's observations by direct current polarography.[9] At pH 8.3, the peak height did not change appreciably, but the potential shifts to -1.25 V.

The addition of bisulfite to the carbonyl group in acrolein destroyed the peak but so did hydrogenation of the double bond--propionaldehyde is not polarographically active at voltages less than -1.4 V vs. S.C.E. The direct current polarographic reduction wave for propionaldehyde in 0.1 M lithium hydroxide did not appear until about -1.9 V.[18] The absence of differential pulse polarographic activity between -0.5 and -1.4V was observed for the acrolein-bisulfite complex in a test solution that was deaerated for 10 min and consisted of 10 ml of 0.50 mg/l of acrolein, 22.5 mg/l of sodium sulfite (sufficient to form the complex with 10 mg/l of acrolein), 1.0 ml of 1.0 M phosphate buffer solution (pH 7.4) and 100 µl of 10% EDTA solution. Since neither the double bond in the acrolein-bisulfite complex nor the carbonyl in propionaldehyde are polarographically active in the -0.5-V to -1.4-V range, then the π-electron system, which includes both, must be involved in the reduction of acrolein. But these observations do not contradict that the reduction may be represented by the equations

$$CH_2{=}{=}CH - CHO + 2H^+ + 2e \longrightarrow CH_3{-}CH_2{-}CHO \qquad (2)$$

$$CH_2{=}{=}CH - CHO + 4H^+ + 4e \longrightarrow CH_3{-}CH_2{-}CH_2OH \qquad (3)$$

Equation (2) represents the first peak, which is given by figure 1, and equation (3) represents the second peak.

Oxygen -

Dissolved oxygen greatly reduces the sensitivity attainable by differential pulse polarography. For best sensitivity it is absolutely necessary to remove traces of oxygen from the test solution and from the nitrogen used to sparge the solution. The gas system must be purged overnight before commencing analysis. We conducted experiments to determine the optimum outgassing time and found that 10 min produced the best sensitivity. The reference electrode must be isolated by a salt bridge from the solution being measured to eliminate sloping baselines caused by oxygen entry, leakage of salt solution from the reference electrode, or both.

Physical Interferences

Decomposition -

In the polarographic determination of acrolein, peak heights decreased by about 10% on the second polarographic scan. For best results, each operator should carefully reproduce the outgassing period and the quiescent time before beginning each scan.

Instrumentation -

Instrument settings greatly affect the sensitivity[16] of differential pulse polarography. The drop time, the pulse modulation amplitude, and even the scan rate change the height of the peak.

VOLTAMMETRY AT POSITIVE POTENTIALS WITH THE GLASSY CARBON ELECTRODE

Several experiments were conducted to develop a method for analyzing acrolein by voltammetry at positive potentials using the glassy carbon electrode. Glassy carbon, a recently developed electrode material,[34] is available in electrode form from Princeton Applied Research Corporation.[19] Operating at positive potentials usually requires no deaeration, as opposed to the lengthy deaeration needed at negative potentials.[18]

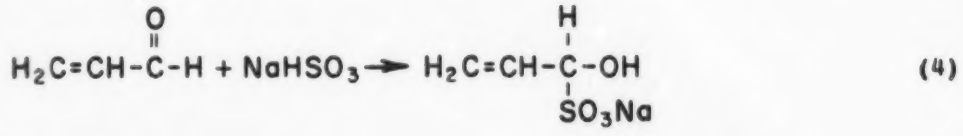
Experimentation led to an indirect determination of acrolein by formation of the acrolein-sulfite complex and

voltammetric measurement of unreacted sulfite at about +0.6 V vs. S.C.E. (NaCl) with the glassy carbon electrode (see figure 3). The electrolyte is buffered at pH 7.2 with 0.09 M phosphate. Lengthy deaeration is unnecessary, but the detection limit is only 10 mg/l (as compared to 0.05 mg/l with the polarographic method).

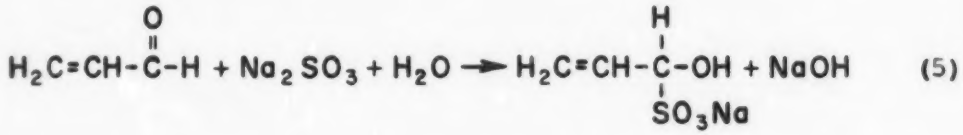
Before each of the experiments discussed below, the glassy carbon electrode was cleaned as described in the "Procedure" section. The instrument settings are also given in the "Procedure" section. The first experiments were performed to determine whether acrolein would oxidize in the voltage range from -0.2 V to about +1.2 V. A series of test solutions consisted of 10.0 ml of a 100-mg/l standard acrolein solution plus 1.00 ml of either 1.0 M phosphate buffer solution (pH 7.4), 1.0 N sodium hydroxide, or 1.0 N sulfuric acid. The test solutions were sparged with nitrogen for 10 min before a slow voltammetric scan was begun in the differential pulse mode at -0.2 V vs. S.C.E. (NaCl) and 100 μA full scale.

No polarographic peaks were observed between -0.2 and +1.1 V vs. S.C.E. (NaCl) for any of the solutions. Because acrolein seemed to be inactive over the wide range of pH values examined, further testing was abandoned.

Acrolein readily forms a sulfite complex,[1,22] as seen in equations (4) and (5).[23]



(4)



(5)

This suggests the basis for a determination of acrolein either directly in the form of the complex or indirectly by measurement of the unreacted sulfite. Equations (4) and (5) were derived from the general reactions of sulfite forms with aldehydes and from our finding, discussed in the experimental section, that one sulfite molecule reacts with

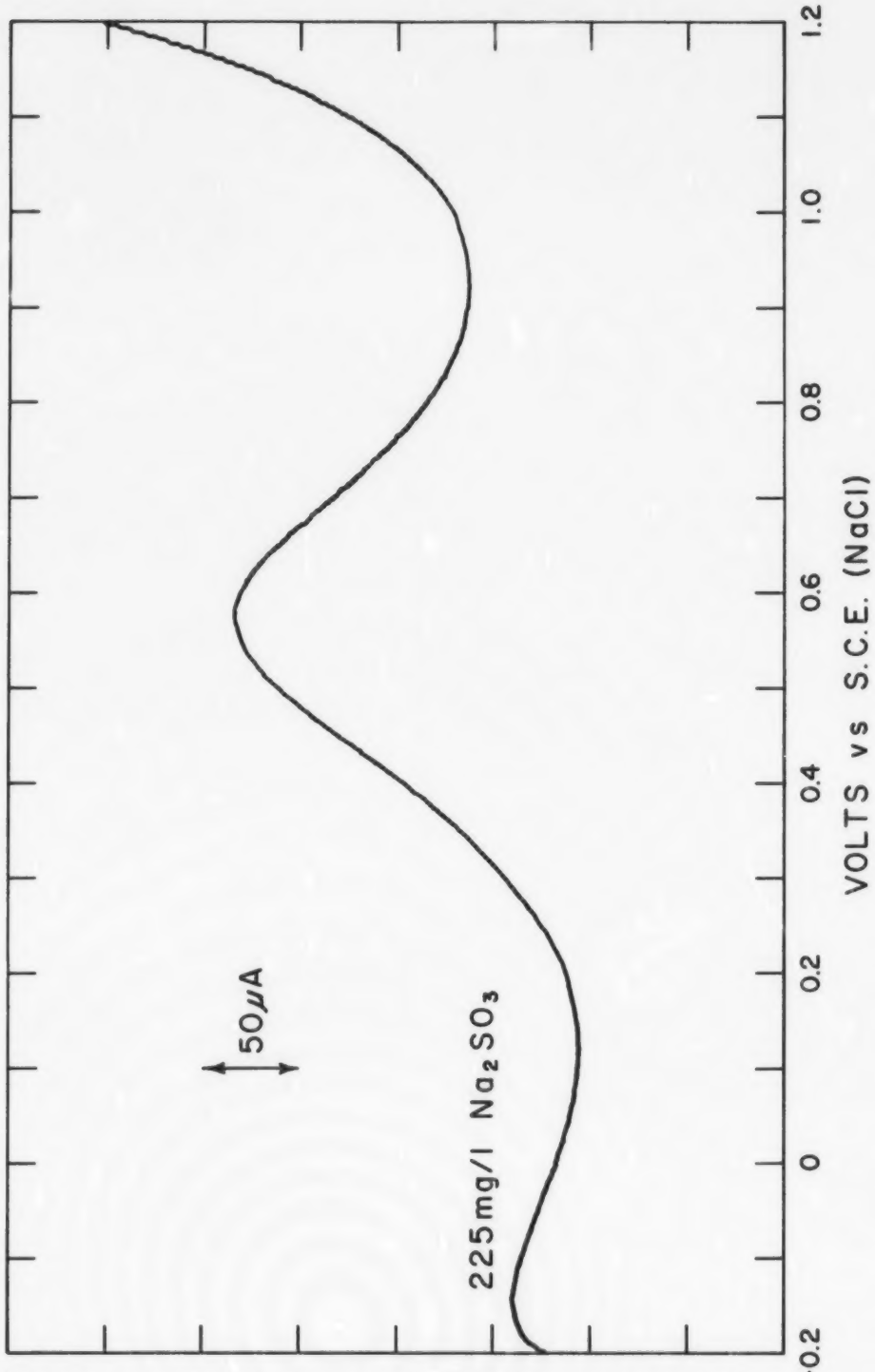


Figure 3. Voltammogram of Sulfite at pH 7 with Glassy Carbon Electrode

one molecule of acrolein. Because acrolein can react with sodium sulfite or sodium bisulfite, either form of sulfite can be used in studying the reaction. The ionization constants[35] of sulfite are such that the chemical forms change, with sulfur dioxide predominating at pH 1, bisulfite at pH 4, and sulfite in neutral and alkaline solutions.

Exploratory studies were conducted on the voltammetry of sodium sulfite alone and in the presence of acrolein. The study was conducted with the glassy carbon electrode at pH 1, 4, 7, and 13. The first experiment was made on a test solution consisting of 10.0 ml of 225 mg/l of sodium sulfite and 1.00 ml of 1.0 M phosphate buffer solution (pH 7.4). The solution was sparged for 10 min. The voltammogram, shown in figure 3, exhibited a large peak at +0.58 V vs. S.C.E. (NaCl), which is approximately the potential predicted from the standard potential.[21] The peak height was 146 μA. In contrast, there was no peak on the voltammogram of a test solution containing 225 mg/l of sodium sulfite and 100 mg/l acrolein, an amount stoichiometrically equivalent to the amount of sulfite. This indicated that the sulfite reacted quantitatively with acrolein to form a polarographically inactive complex.

When the deaeration time was decreased from 10 min to 5, 2, and 1 min, the peak current decreased to 134, 137, and 137 μA, respectively. With no deaeration, it was 100 μA. The slope of the background current did not change appreciably as the deaeration time was decreased. Because the peak heights were essentially unaffected by additional deaeration, subsequent experiments on sulfite were conducted with 1 min of outgassing.

The voltammogram of a test solution containing 10.0 ml of 225 mg/l of sodium sulfite and 1.00 ml of 1.0 N sodium hydroxide exhibited a peak at +0.59 V vs. S.C.E. (NaCl), see figure 4. The peak height of 136 μA approximately equaled that found at the neutral pH of the 0.09 M phosphate buffer solution. In contrast, the addition of 100 mg/l of acrolein resulted in a peak current of only 7 μA at +0.59 V. This indicated that the acrolein-sulfite complex is not decomposed in dilute alkali, at least not at this concentration (91 mg/l, when dilution with the sodium hydroxide is considered).

The next set of experiments was the same as the previous one except that 1.00 ml of 1.0 M phosphate buffer solution (pH 4.2) was added instead of the sodium hydroxide. Under these conditions, however, the sulfite peak--or, more

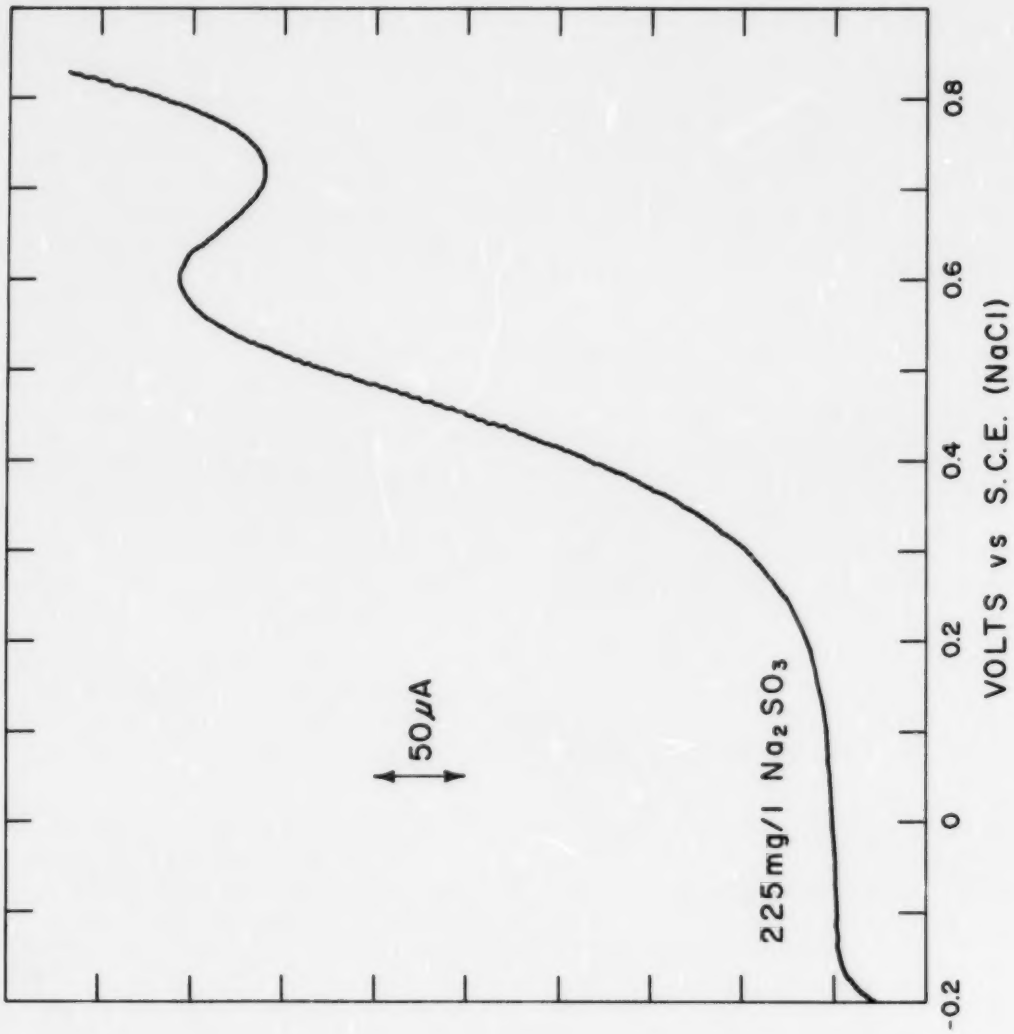


Figure 4. Voltammogram of Sulfite at pH 13 with Glassy Carbon Electrode

correctly, the bisulfite peak, which predominates at pH 4[35]--appeared at +0.79 V, +0.21 V more positive than at pH 7.4 (see figure 5). The peak height for sulfite alone was 152 μA. As at pH 7.4, the sulfite peak was nearly eliminated in the presence of an equivalent amount of acrolein. The stoichicmetric quantity of acrolein decreased the height of the sulfite peak to 7 μA.

In the final experiment, 1.00 ml of 1.0 N sulfuric acid was added to 10.0 ml of a 225 mg/l sulfite solution. A peak for sulfurous acid, the conjugate acid form of sulfite, appeared at +1.06 V (see figure 6). The height of this peak was 196 μA. The stoichiometric amount of acrolein did not eliminate this peak; the peak decreased slightly to 183 μA.

These experiments showed that sulfite quantitatively or nearly quantitatively reacted to form a complex with acrolein between pH 4 and pH 13. The complex decomposes, almost quantitatively, at about pH 1. Both acidic and basic solutions gave polarograms with steeply sloping baselines. The best polarograms with the best baselines were obtained in solutions buffered with 0.09 M phosphate at pH 7.4 (see figures 3-6).

Because the neutral phosphate system was the best for measuring acrolein by determining unreacted sulfite, we decided to determine the detection limit. The detection limit is about 10 mg/l acrolein, which is equivalent to 22.5 mg/l of sodium sulfite. The peak height for 22.5 mg/l of sodium sulfite was approximately 6 μA. The sensitivity might be improved with the graphite electrode impregnated with styrene and irradiated with cobalt 60.[36]

Formation of the acrolein-sulfite complex might be effective for neutralizing the toxicity of acrolein. It is thought that the complex is not toxic.[4]

Voltammetric oxidation of sulfite at the glassy carbon electrode in neutral solutions may be applicable to monitoring sulfur dioxide in air. The detection limit of 22.5 mg/l for sodium sulfite achievable by this method corresponds to 11.4 mg/l of sulfur dioxide. If the sulfur dioxide in a 100-liter sample of air were trapped with 100% efficiency in 1.00 ml of buffered electrolyte, this represents a concentration of 0.044 μl/l (25 °C, 760 mm Hg at 0 °C, 1.013×10^5 pascal, Pa) of sulfur dioxide.

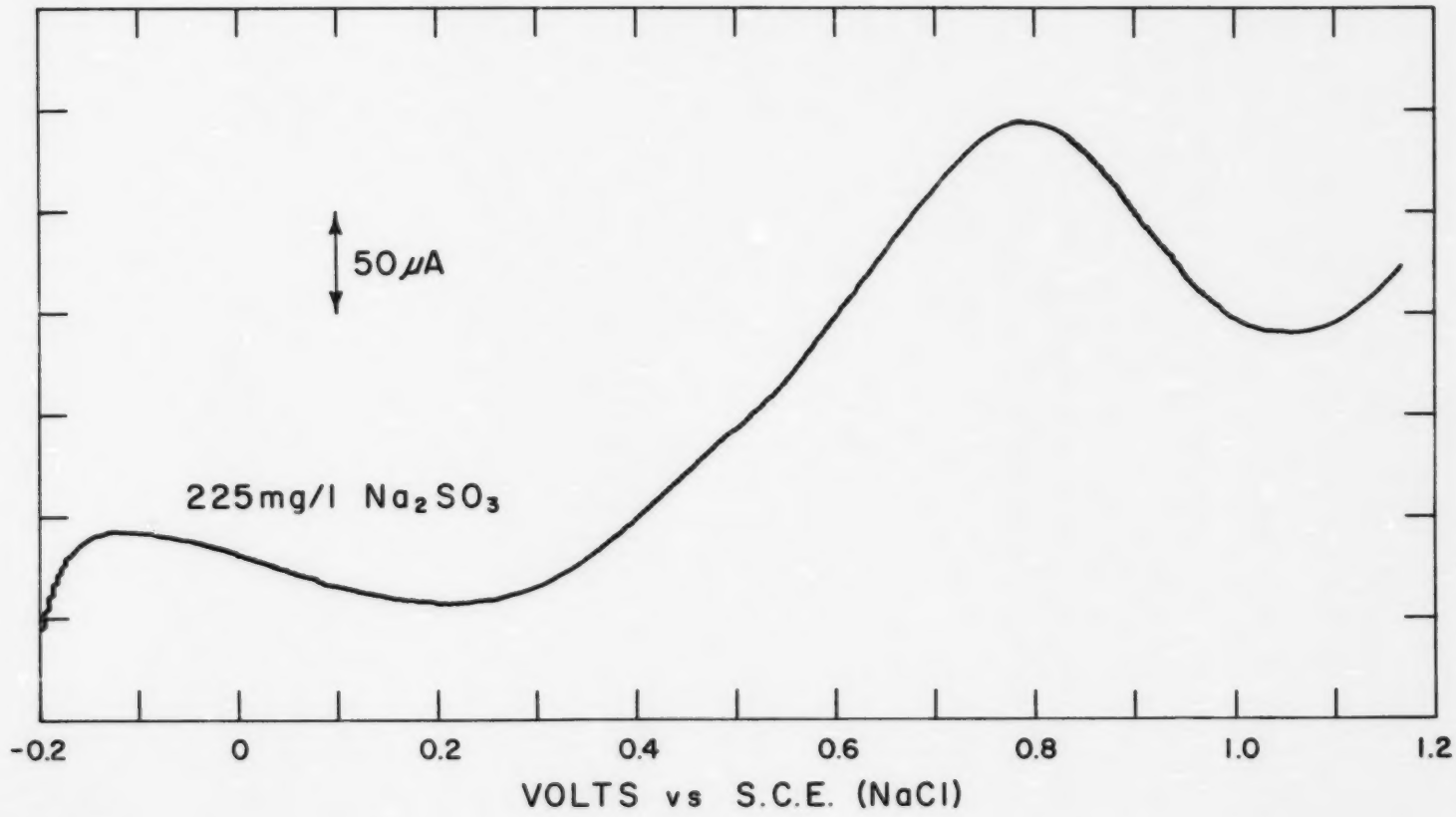


Figure 5. Voltammogram of Sulfite at pH 4 with Glassy Carbon Electrode

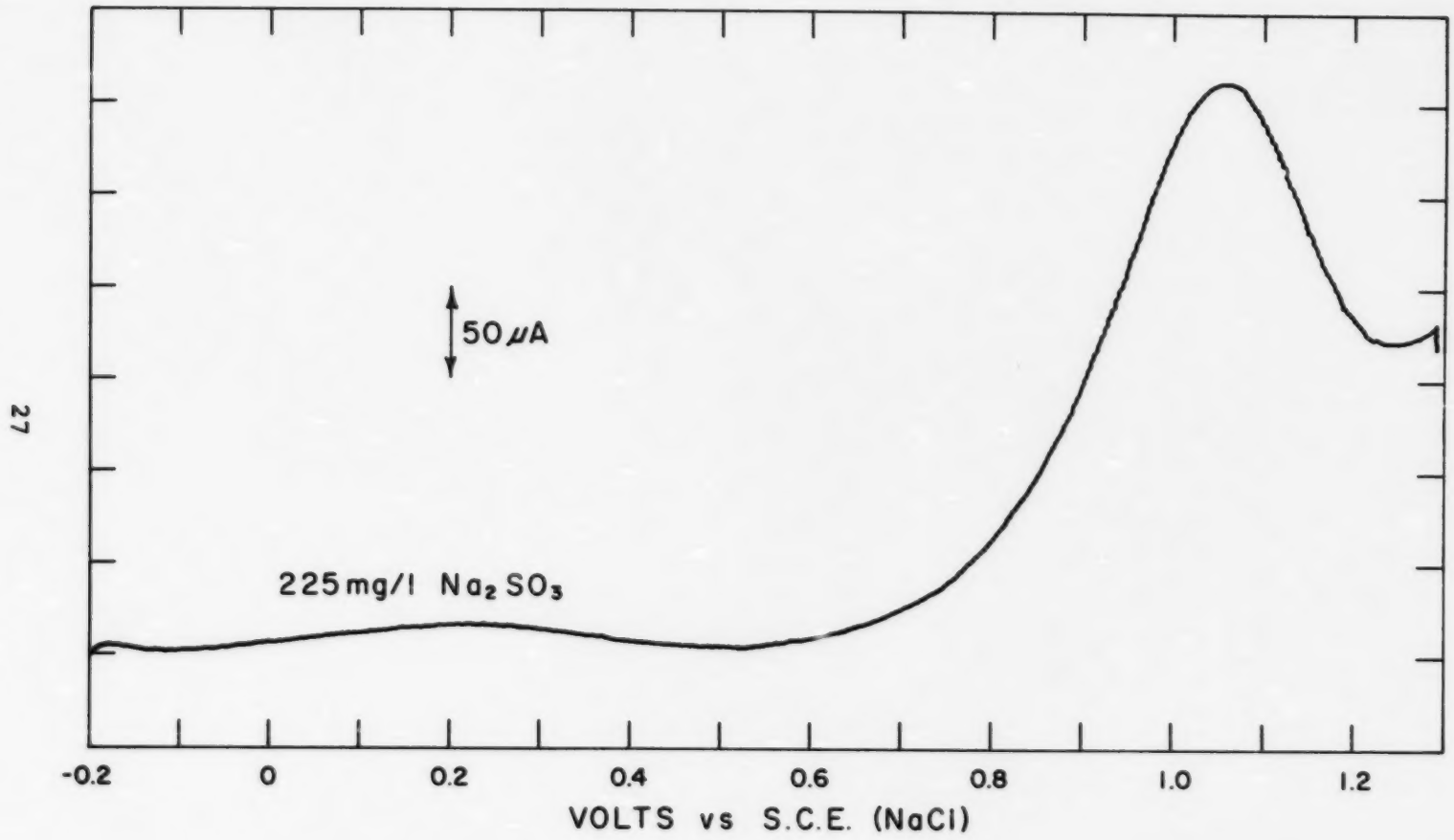


Figure 6. Voltammogram of Sulfite at pH 1 with Glassy Carbon Electrode

PRESERVATION WITH SULFITE

The purpose of these studies was to develop a technique for preserving water samples for several days while they are shipped to the laboratory for analysis of low levels of acrolein. While high levels of acrolein, 2-8 mg/l, can be preserved with excess sulfite,[28] there was no information on low-level preservation or analysis of acrolein in concentrations of 0.05-0.5 mg/l with excess sulfite added.

Initial efforts were toward a direct measurement of acrolein released from its complex with sulfite. Because voltammetry at the glassy carbon electrode is not sensitive enough to measure acrolein at the 0.5 mg/l level and below, the polarographic procedure (voltammetric procedure at the dropping mercury electrode) was modified in attempts to find suitable conditions for a direct analysis. No entirely adequate polarographic method was found for analyzing low concentrations of acrolein in the presence of excess sulfite through the experiments described below.

All of the polarographic scans in the following experiments were conducted under nearly the same conditions as those in the recommended method with the exception that, in some instances, the initial voltage was changed to assure that no polarographic peaks were missed.

The first experiment was performed on a test solution consisting of 0.5 mg/l of acrolein, 22.5 mg/l of sodium sulfite (sufficient to form the complex with 10 mg/l of acrolein), 1.00 ml of 1.0 M phosphate buffer solution (pH 7.4), and 100 µl of 10% EDTA solution. After the sample was deaerated for 10 min, the polarogram was recorded beginning at -0.500 V. No significant polarographic peaks appeared between -0.5 and -1.4 V, and it was concluded that the acrolein-sulfite complex is not polarographically active at pH 7.4.

This experiment was repeated with 1.00 ml of 1.0 M sodium hydroxide in place of the phosphate buffer. No polarographically active peaks were observed between -0.9 and -1.55 V.

With 1.00 ml of 1.0 N sulfuric acid substituted for the sodium hydroxide, a peak for acrolein was observed at -0.88 V. The peak height was 344 nA (see figure 7). The height was very difficult to measure because the baseline sloped considerably and increased rapidly at about -1 V. In a fourth test solution containing no sodium sulfite, the

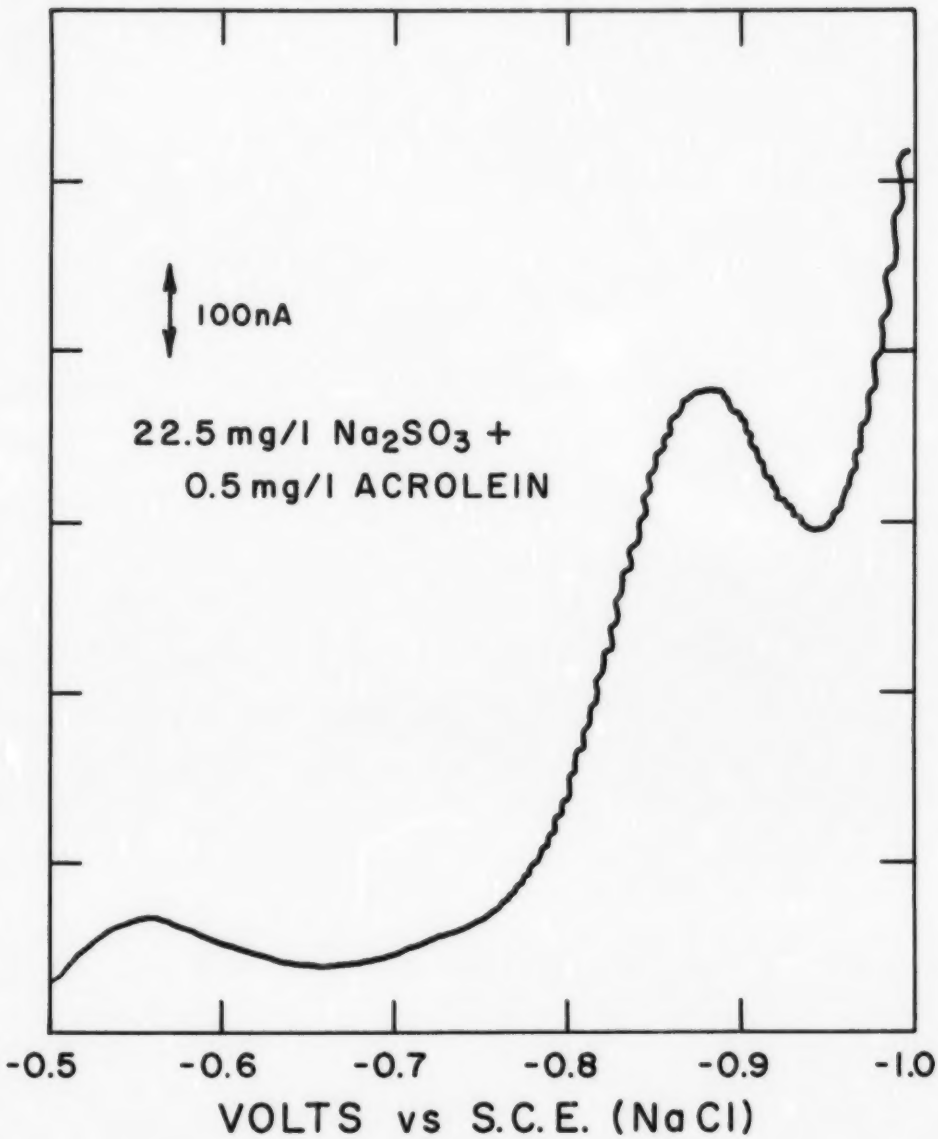


Figure 7. Polarogram for Acrolein in Excess Sulfite at pH 1 with Dropping Mercury Electrode

peak current for acrolein was 592 nA (see figure 8). However, the baseline still sloped considerably and increased rapidly at about -1 V. Because of the unfavorable baseline pH (the most favorable at the time), this technique was unsatisfactory for measuring acrolein at the 0.5 mg/l level. Had a microprocessor (Princeton Applied Research Model 374 Polarographic Analyzer System) been available to correct digitally for the steeply sloping baseline caused by the sulfuric acid blank, this electrolyte might well have been suitable for precisely determining acrolein in samples preserved with sulfite.

Because a polarographic peak was observed for 0.5 mg/l of acrolein in dilute sulfuric acid in the presence of a 20-fold excess of sodium sulfite, sulfite might be converted to sulfur dioxide in dilute acid and removed by sparging with argon, allowing the determination of the regenerated acrolein at neutral pH with the recommended polarographic method.

To test this approach, a synthetic solution was prepared to simulate a water sample preserved for acrolein analysis. To 100 ml of reagent water was added enough acrolein to produce a concentration of 0.5 mg/l, enough sodium sulfite to produce a concentration of 22.5 mg/l, and 1.00 ml of 1.0 M phosphate buffer solution (pH 7.4). There was enough sulfite present to form a complex with 10 mg/l of acrolein. The addition of 3.0 ml of 1.0 N sulfuric acid lowered the pH of this solution from about 7.2 to 2.1. Argon (presaturated with water), delivered vigorously through a coarse, sintered glass frit, was used to deaerate the solution for various lengths of time. The amount of acrolein in the solution was determined by the recommended procedure. Low recovery rates resulted, even after the optimum outgassing time of 20 min. At most, only 15% of the acrolein was recovered. Therefore, this approach was abandoned.

The last approach was an attempt to release acrolein from the sulfite complex by distillation from an alkaline solution. To 100 ml of a solution containing 0.5 mg/l of acrolein, 22.5 mg/l of sodium sulfite, and 1.0 ml of phosphate buffer solution (pH 7.4) was added 10 ml of 1.0 N sodium hydroxide. In a closed system, the entire solution was heated in a boiling-water bath while being sparged with argon. The gas from the system was scrubbed through a 10-ml impinger with a sintered glass disc at the inlet. The impinger contained 10 ml of reagent water, 1.0 ml of 1.0 M phosphate buffer (pH 7.4), and 100 µl of 10% EDTA solution. After 20 min of sparging, the solution in the impinger was

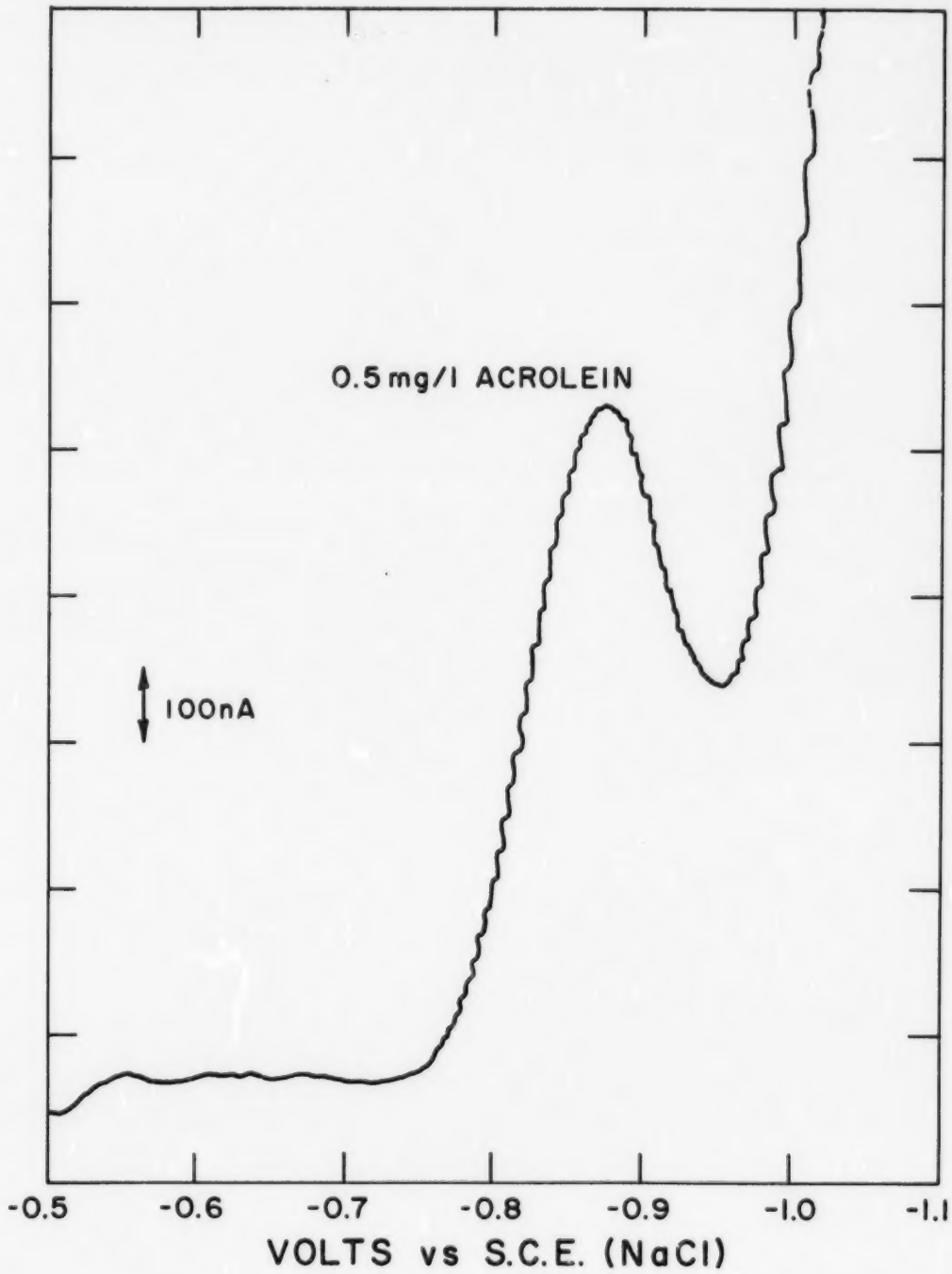


Figure 8. Polarogram for Acrolein at pH 1 with Dropping Mercury Electrode

analyzed for acrolein by the recommended procedure. About 17% of the acrolein was recovered in this attempt to release the acrolein from the bisulfite complex.

Sulfite may very well be an effective preservative for low concentrations of acrolein in water samples, but no method was found to find a way to recover acrolein from solutions containing sulfite.

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"Differential Pulse Polarographic Determination of Acrolein in Water Samples" by Lyman H. Howe was accepted on September 3, 1976, by Analytical Chemistry for tentative publication in December of 1976.

GLOSSARY

Acrolein demand - Quantity of acrolein dissipated in the test water.

A - Ampere.

c- - Centi-, $X10^{-2}$ (as a prefix, e.g., cm).

d - Mean of the differences between paired observations.

°C - Degrees Celsius (centigrade).

EDTA - Ethylenediaminetetraacetic acid.

g - Grams.

hr - Hour.

l - Liter.

m - Meter.

μ- - Micro-, $X10^{-6}$ (as a prefix, e.g., l).

m- - Milli-, $X10^{-3}$ (as a prefix, e.g., mm).

min - Minute.

M - Molar, mole per liter.

n- - Nano-, $X10^{-9}$ (as a prefix, e.g., ng).

N - Normal, equivalent per liter.

% - Percent.

Pa. - Pascal.

Polarography - Voltammetry at the dropping mercury electrode.

PAR - Princeton Applied Research.

t - Student-t statistic.

TVA - Tennessee Valley Authority.

V - Volt.

V vs. S.C.E. - Volts versus a calomel electrode filled with saturated potassium chloride.

V vs. S.C.E. (NaCl) - Volts versus a calomel electrode filled with saturated sodium chloride.

w/v - Weight expressed as a fraction of total volume.

APPENDIX

RECOMMENDED POLAROGRAPHIC PROCEDURE (VOLTAMMETRIC PROCEDURE AT DROPPING-MERCURY ELECTRODE) FOR ACROLEIN ANALYSIS

REAGENTS

Acrolein Stock Solution

With a weighing pipet, transfer about 1 g of purified acrolein (weighed to the nearest 0.01 mg) to a 1000-ml volumetric flask containing 500 ml of reagent water. Dilute the solution to 1000 ml and mix. Prepare a fresh solution daily.

Acrolein Standard Solution, 100 mg/l

Prepare this solution by appropriate dilution of the stock solution.

Phosphate Buffer Solution, pH 7.4

Solution A--Dissolve 174.18 g of dipotassium hydrogenphosphate in reagent water and dilute to 1000 ml. This 1.0 M solution has a pH of 9.3.

Solution B--Dissolve 136.09 g of potassium dihydrogenphosphate in reagent water and dilute to 1000 ml. This 1.0 M solution has a pH of 4.2.

Phosphate buffer solution, pH 7.4--Mix 300 ml of solution A with 100 ml of solution B.

EDTA Solution, 10% (w/v)

Dissolve 25 g of disodium ethylenediaminetetraacetic acid dihydrate and dilute to 250 ml with reagent water. Heat and stir the solution if necessary to complete dissolution of the salt. If dissolution is incomplete, filter the solution, and discard the first 10 ml.

INSTRUMENTAL

The natural drop time of the capillary should be approximately 3 sec in 0.09 M phosphate buffer solution (pH 7.4). Use a carbon or platinum counter electrode and a calomel reference electrode filled with saturated sodium or potassium chloride. Use a salt bridge to isolate the reference electrode from the test solution.

The following typical settings are for a PAR 174 polarographic analyzer with mechanical drop timer: drop time, 2 sec; scan rate, 2 mV/sec; display direction, positive; scan direction, negative; initial potential, -0.900 V; range, 1.5 V; sensitivity, 0.5 µA for 0.1 mg/l acrolein, 1 µA for 0.3 mg/l, and 2 µA for 0.5 mg/l; modulation amplitude, 100 mV; operation mode, differential pulse; output offset, negative settings as required. When using the PAR 174 in combination with the Houston Omnigraphic 2200-3-3 Recorder, adjust recorder Y-axis to 1 V/in. (0.039 V/mm) and X-axis to 100 mV/in. (3.94 mV/mm). Other polarographic instruments probably can be substituted without loss in sensitivity if they provide differential pulse of pulse polarographic modes with sufficiently slow scan rates.[17]

PROCEDURE

To 10.0 ml of sample, add 1.00 ml of phosphate buffer solution (pH 7.4) and 100 µl of 10% EDTA solution. Place the solution in the polarographic cell. Deaerate for 10 min with oxygen-free nitrogen. Electrically connect solution. Wait a minute. Make a polarographic scan between -0.9 and -1.5 V vs. S.C.E. (NaCl). The peak appears at about -1.2 V. Compare the peak currents with those for standard solutions similarly prepared. The procedure is applicable to acrolein concentrations from 0.05 to 0.5 mg/l.

The acrolein consumption (demand) of the sample is determined by measuring the acrolein remaining after the contact period and subtracting it from that added initially.